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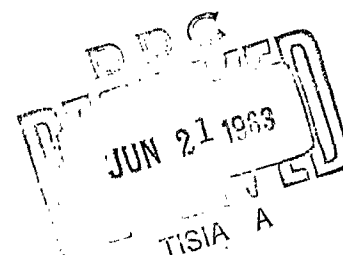
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THE BEHAVIOR OF MONOLAYERS OF PROGRESSIVELY FLUORINATED FATTY ACIDS ADSORBED ON WATER

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ABSTRACT

A study has been made on the force-area, surface potential-area, and surface moment-area relations of monolayers of two series of progressively fluorinated fatty acids spread on water at various pH values. The series were n-heptadecanoic acids with substitutions in the 17-position of perfluoromethyl, perfluoropropyl, perfluoropentyl, and perfluoroheptyl groups, and n-undecanoic acids with substitutions in the 11-position of perfluoroheptyl, perfluorooctyl, and perfluorodecyl groups. In both series the stability of the monolayers at all pH values falls off rapidly with progressively shorter perfluoro segments. The compressed films of all stable acids are in the liquid-condensed state, indicating limiting areas per molecule of $36A^2$ to $38A^2$. The change in surface potentials of all films is larger than those of any aliphatic acid and shows that the dipole is oriented in the opposite direction. By use of the Helmholtz equation the vertical components of the apparent dipole moment were ascertained from the potentials and it was possible to compute, under a given set of conditions, the values of the vertical component of the partially fluorinated chain only. The results were interpreted in terms of orientation and packing of the adsorbed molecules, steric hindrance due to the bulky perfluoro segments, and electrostatic repulsion.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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THE BEHAVIOR OF MONOLAYERS OF PROGRESSIVELY
FLUORINATED FATTY ACIDS ADSORBED ON WATER

INTRODUCTION

Previous investigations (1,2) at this Laboratory have been concerned with the surface-chemical properties of adsorbed monolayers of molecules comprising a single linear chain of 16 $-CH_2-$ groups terminated on one end by a $-CF_3$ group and on the other end by a carboxylic acid or an amino group. Shafrin and Zisman (1) suggested the presence of a strong dipole in the $-CH_2-CF_3$ linkage in order to explain the small effect of fluorinating the ω-carbon atom on the wettability of the condensed monolayer adsorbed on polished glass or metal substrates. Fox (2) proposed that the same dipole through weakening of the cohesive forces also caused a film expansion in the insoluble mono-layers spread on water. More recently Shafrin and Zisman (3) investigated the wetta-bility of monolayers adsorbed on metals using a series of ω-(n-perfluoroalkyl) hepta-decanoic acids and found that the effect on liquid adhesion of the uncompensated dipole at the $-CH_2-CF_2-$ linkage became negligible only when it was located at least six carbon atoms from the ω-carbon atom. The present study reports the mechanical and electrical properties of insoluble monolayers on water using the same family of progressively fluorinated fatty acids (the 17-heptadecanoic acids) as well as an analogous family, the perfluoroalkyl substituted 11-undecanoic acids.

EXPERIMENTAL MATERIALS AND PROCEDURES

The organic acids studied were highly purified, white, crystalline solids. The ω-trifluorostearic acid was prepared by Gavlin (4) and all other fluorinated acids were prepared by Brace (5). As in the study reported earlier (3), these compounds were pure enough to be used as received. The stearic acid used for purposes of comparison was Eastman "White Label" grade (mp = 69.5°C). Table 1 lists the compounds studied, the number (n) of carbon atoms in the fluorinated chain, the melting point, and a conveniently abbreviated code name which will be used hereafter in this report.

The solvent used to spread the acid on water was n-hexane which had previously been purified by repeated percolation through an adsorption column packed with acti-vated silica gel and alumina. Concentrations of the fluorinated acids in hexane ranged from 1.0×10^{-4} to 6.1×10^{-4} g/ml solvent. Each solution was delivered dropwise to the clean water surface of the film balance with a calibrated, self-adjusting, micropipet in a volume selected to give a condensed film occupying from 200 to 240 cm^2. The modified Langmuir-Adam film balance used was made of a single piece of Pyrex glass sand-blasted* to form a trough 0.2 cm deep, 73 cm long, and 12 cm wide. Before the experi-ments the trough and the movable Pyrex barriers were cleaned with a hot concentrated nitric-sulfuric acid solution, rinsed thoroughly with distilled water, and dried in a dust-free atmosphere. A coating of white paraffin wax (melting range 65°-70°C) was applied while molten to the tray rim and barriers to render them hydrophobic. Film pressures were measured with a Cenco du Nouy torsion head equipped with a piano steel torsion wire (torsion constant 0.3578 degree per dyne/cm), a lightly paraffined mica float, and two end loops of thin polyethylene ribbon.

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*As manufactured to order by Fred S. Hickey Corp., Chicago, Illinois

Table 1
Molecular Formulas and Code Designation of the Fluorinated Fatty Acids

Compound	n	Melting Point (°C)	Code
$F(CF_2)_n - (CH_2)_{16} COOH$			
17-(perfluoroheptyl) heptadecanoic acid	7	91-92	7F-16H acid
17-(perfluoropentyl) heptadecanoic acid	5	77-79	5F-16H acid
17-(perfluoropropyl) heptadecanoic acid	3	73-74.5	3F-16H acid
17-(perfluoromethyl) heptadecanoic acid	1	70.0-70.5	1F-16H acid
Stearic acid	-	69.5	17H acid
$F(CF_2)_n - (CH_2)_{10} COOH$			
11-(perfluorodecyl) undecanoic acid	10	111-112	10F-10H acid
11-(perfluorooctyl) undecanoic acid	8	89-90	8F-10H acid
11-(perfluoroheptyl) undecanoic acid	7	82-83	7F-10H acid

The surface potential change (ΔV) due to the adsorption of the monolayer on the water was measured by the vibrating condenser method (6) using an aged stainless steel electrode, 3.7 cm in diameter, which was held close to the surface of the water in the trough and driven at 200 cycles/sec by being attached to the diaphragm of an earphone connected to an ac generator. Because of the contact potential difference between the electrode and the water, an ac signal was generated by the vibrating condenser which was passed through a 200-cycle bandpass General Radio high-gain amplifier (Model 1231-B) and then was detected by an RCA high-sensitivity, vacuum tube voltmeter (Model WV-74A). The contact potential difference was measured by applying an equal and oppositely directed potential difference to the two electrodes with a Rubicon potentiometer so as to give a null in the ac signal. This system had a sensitivity of ± 2 mv even when using the convenient condenser air gap of 2 mm.

Aqueous substrates were prepared from water distilled once through a tin-lined still and then twice through an all-quartz still. The water obtained, when in equilibrium with CO_2 of the air, had a pH of 5.8. Appropriate additions of C.P. grade H_2SO_4 or KOH were made in order to obtain various pH values of the aqueous substrate. Film balance experiments were all carried out at $20°C \pm 0.2°C$. The more highly fluorinated acids were so slightly soluble in hexane that they had to be stored at $25°C$ or above to keep them from precipitating. At time of delivery to the water surface, however, all of these solutions were at a temperature of $20°C$.

CHOICE OF SPREADING SOLVENT

A search for a suitable spreading solvent showed that most of the conventional solvents were unable to dissolve the partially fluorinated acids, especially the higher homologs. Previous investigations (7-10) have established that the nature of the spreading

solvent can exercise a considerable influence on the properties of an adsorbed mono-layer. For example, benzene was found to remain in the monolayer even under film pressure, and it caused an increased expansion in the low-pressure regions before the formation of liquid-condensed films. Hexane or petroleum ether were found more suitable as spreading solvents; a short-chain alcohol also was satisfactory despite its high water solubility. In view of these findings, a brief study was made of the effect of varying the spreading solvent on the film pressure (F) vs area per adsorbed molecule (A) of these fluorinated acids.

Figure 1 graphs the results obtained when the 7F-16H acid was spread on water at pH 2.2 from each of four solvents; similar graphs were obtained with the other fluorinated acids studied. Two sets of curves are seen; one set was obtained when the spreading solvents were hexane or petroleum ether, and the other set when they were acetone or isopropyl alcohol. The two sets of curves are roughly parallel except that the latter set exhibits an extended gaseous region and is displaced by about $8A^2$ to the left of the former, indicating smaller limiting areas per molecule. Because of the water solubility of the acetone and isopropyl alcohol, it was suspected that these solvents might have carried the organic acid into the aqueous substrate. This was verified when it was found that the clean hydrophilic platinum foil, employed as an electrode for measuring the surface potential and fully submerged in the film trough, became hydrophobic after several runs with acetone or isopropyl alcohol as the spreading solvent, but remained hydrophilic when hexane or petroleum ether was used instead. Therefore, hexane was chosen as the most suitable spreading solvent for this investigation, in spite of its lower solvent power for the more highly fluorinated acids.
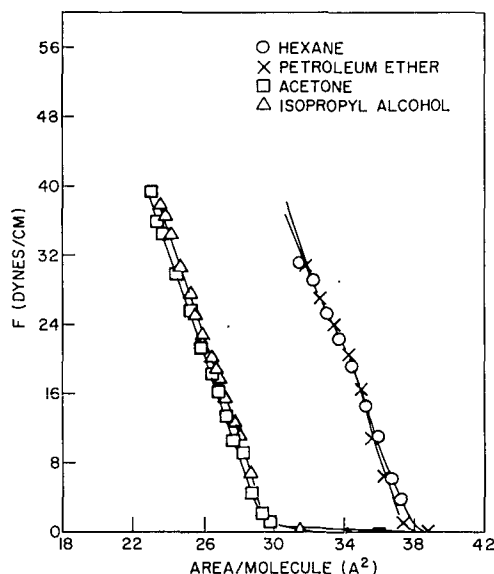

Fig. 1 - Effect of spreading solvents on monolayers of 7F-16H acid on substrate of pH 2.2

FILM PRESSURE VS AREA PER MOLECULE

In Figs. 2 and 3 are F-vs-A graphs for each of the seven fluorinated acids when spread on an aqueous substrate of pH 2.2. In the undecanoic acid series (Fig. 2), the compound with the largest number of $-CF_2-$ groups (10F-10H acid) supported the highest film pressure, 55 dynes/cm, the next lower member (8F-10H acid) collapsed at 43 dynes/cm, and the lowest member (7F-10H acid) collapsed at only 9 dynes/cm. Each curve was reversible at all film pressures except close to the collapse value. Any member of this series of acids containing fewer than seven $-CF_2-$ groups could not be studied with the film balance because its collapse pressure was too low. An analogous decrease in film stability occurred in the family of substituted heptadecanoic acids (Fig. 3); the highest collapse pressure (37 dynes/cm) was exhibited by the 7F-16H acid, which has the largest number of $-CF_2-$ groups, and the lowest collapse pressure (6 dynes/cm) was encountered by the member with the smallest number of $-CF_2-$ groups (1F-16H). Again the F-vs-A curves were reversible over the entire range of film pressures except close
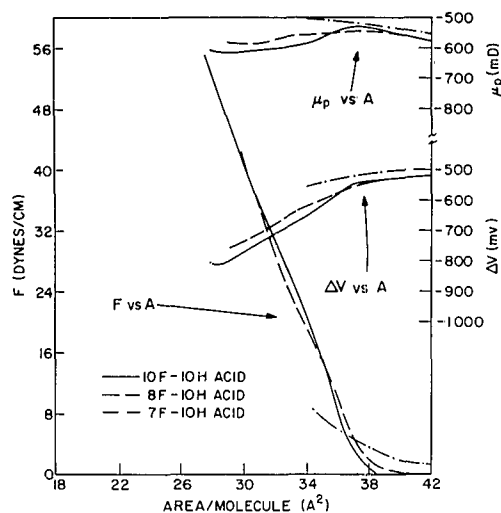
Fig. 2 - Properties of monolayers of
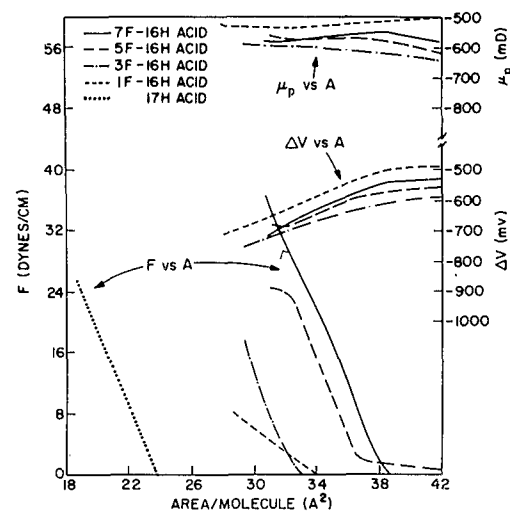nF-10H acids spread on substrate of
pH 2.2

Fig. 3 - Properties of monolayers of
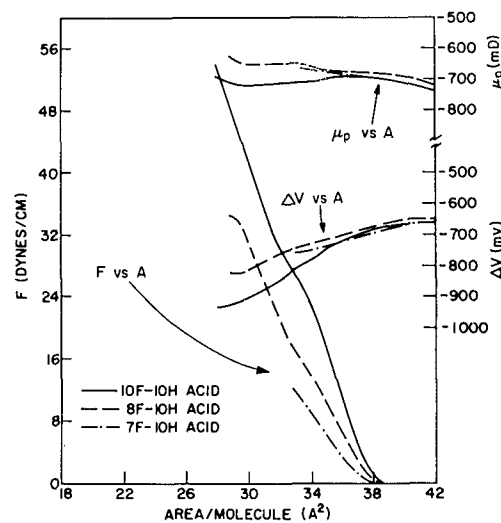nF-16H acids spread on substrate of
pH 2.2

Fig. 4 - Properties of monolayers of
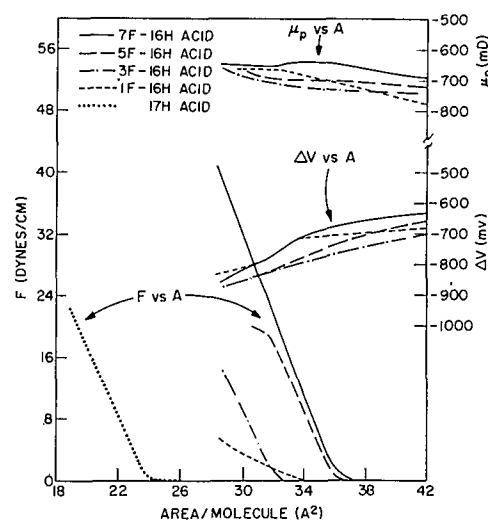nF-10H acids spread on substrate of pH
5.8

Fig. 5 - Properties of monolayers of
nF-16H acids spread on substrate of
pH 5.8

to the collapse point. Data obtained under the same conditions using a monolayer of
stearic acid (17H acid) are also graphed in Fig. 3 for comparison.

Figures 4 and 5 show the F-vs-A curves of these two homologous families of insol-
uble compounds when spread on water of pH 5.8, and Figs. 6 and 7 show the results
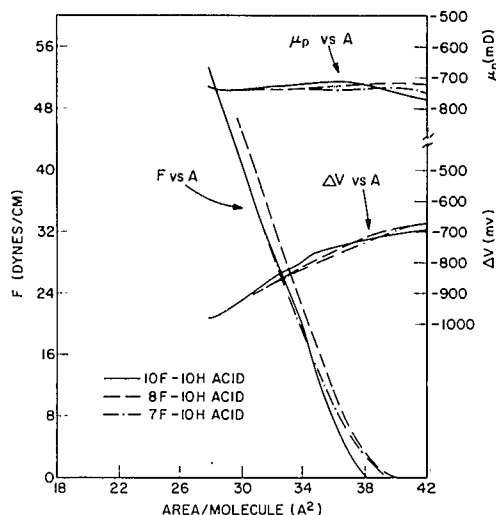
Fig. 6 - Properties of monolayers of nF-10H acids spread on substrate of pH 8.6
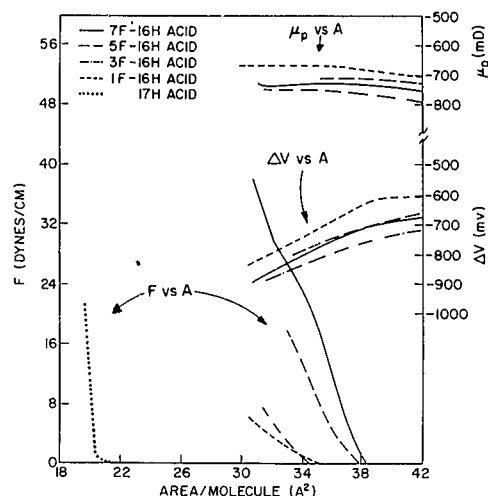

Fig. 7 - Properties of monolayers of nF-16H acids spread on substrate of pH 8.6

obtained at pH 8.6. With the exception of the two shortest members of each family of acids, all curves obtained at each pH are roughly parallel and close to one another, especially at the higher pressures. The minor effect of varying the pH on the shape and position of the F-vs-A curves is exemplified by the behavior of the 10F-10H acid shown in Fig. 8. Thus, regardless of the length of the fluorinated or hydrocarbon segment and the pH of the substrate, the limiting area (A_o) observed with the more stable films varies between $36A^2$ and $38A^2$ per molecule (Table 2). However, areas A as well as film pressure at the collapse point show larger variations. The smallest area for all films $(27.5A^2)$ was observed with 10F-10H acid at pH 2.2; this is close to the cross-sectional area of $25.1A^2$ of a perfluoroalkane chain as measured on a Stuart-Briegleb molecular model.

Fig. 8 - Effect of pH on properties of 10F-10H acid monolayer spread on aqueous substrate

From the slopes of the F-vs-A curves of the more condensed monolayers, it is found that the compressibility $(-1/A)(\partial A/\partial F)$ of the 10F-10H acid film ranges from 0.0054 to 0.0062 and is of the same magnitude for the other longer chain acids. This falls within the range of compressibilities of the liquid-condensed monolayers of fatty acid reported by Harkins (11), and hence it would appear that these fluorinated monolayers are all liquid-condensed up to the collapse pressure. This inference was proved correct by some simple spreading experiments on these monolayers using a film trough covered with a duplex film of oxidized "indicator oil" (12) in order to be able to see the boundary
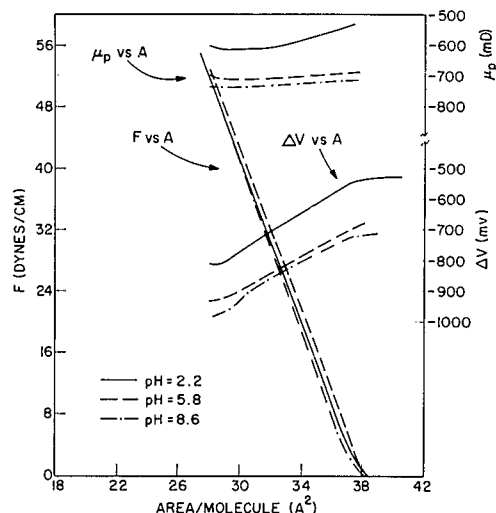
of the spread monolayer of fluorinated acid. Even at the maximum pressures obtained
with the indicator oil (20-25 dynes/cm), no solid-condensed monolayers of these fluori-
nated acids was formed on water of pH 2.2, 5.8, or 8.6. The 10F-10H and 7F-16H acids
formed somewhat more viscous films at pH 8.6 than did the other acids, and the 1F-16H
acid slowly dissolved in the water at all pH values. However, when thorium nitrate (10^{-4}
molal) was introduced into the aqueous substrate under the previously spread monolayer
of each fluorinated acid, the film promptly became rigid at pH 8.6. At pH 5.8 only the
higher homologs (7F-16H and 10F-10H acids) became rigid, and at pH 2.2 none became
rigid. These experiments prove that in the absence of polyvalent metallic ions mono-
layers of these fluorinated acids are liquid-condensed rather than solid films. All can be
transformed at pH 5.8 or higher into solid-condensed films by reaction with appropriate
metallic ions in the aqueous substrate, the condensing effect being greater the greater
the number of $-CF_2-$ groups in the molecule.

The reason why none of these fluorinated acids is able to form solid films on acid
water, despite the large number of carbon atoms per molecule, can be found by stereo-
chemical considerations. The portion of the molecule attached to the polar head consists
of a hydrocarbon chain having a cross-sectional area of $18.5A^2$, whereas the fluorinated
portion at the other end of the molecule has an area of $25.1A^2$, or roughly 35% greater.
Consequently, the adjacent hydrocarbon chains are hindered from cohering to form a
close-packed array. Since the intermolecular forces between adjacent perfluoro alkane
chains are weaker than those of alkane chains, complete cohesion and adlineation of the
perfluoro alkane chains to produce solid films cannot occur until more than ten $-CF_2-$
groups are present in the chain. Possible models of configuration and packing of con-
densed monolayers of such molecules have been discussed by Shafrin and Zisman (3) in
explaining the effect of such adsorbed monolayers on the wettability of solid surfaces.

Large variations found in the collapse pressures for the various acids (Table 2) can
be readily understood since increasing the fluorocarbon chain length always increases
the intermolecular cohesion and hence raises the film stability and collapse pressure in
both homologous series of acids. On comparing the two series (Table 2) it becomes evi-
dent that the 16H series of acids form condensed monolayers, stable under moderate
pressures, even when the fluorocarbon segment contains only one carbon atom, whereas
the 10H series forms stable condensed monolayers only when the fluorocarbon segment
contains seven or more carbon atoms. This would indicate that the hydrocarbon segment
must contain over ten carbon atoms for sufficient chain adlineation to occur in order to
compensate for the steric hindrance caused by the larger cross-sectional area of the
perfluoro group. The shortest total chain length in each series consistent with obtaining
film stability is 18 carbon atoms (1F-16H or 7F-10H acid). Thus, although an 18-carbon,
straight-chain, hydrocarbon acid (stearic acid) forms stable solid-condensed mono-
layers, the progressively fluorinated acids just begin to support pressure at that chain
length, and the higher members compress to form only liquid-expanded or at best,
liquid-condensed films.

The F-vs-A curve of the highest homolog in each series, and to a lesser extent the
next lower acid, evidenced a slight change in slope when F ranged between 12 and 26
dynes/cm, regardless of the pH. The change is significant enough to suggest a shift in
molecular packing, especially since every change in the F-vs-A curve is also reflected
in a corresponding dip in the ΔV-vs-A curve.

Because the F-vs-A results reported by Fox on the 1F-16H acid (2) were not rea-
sonably related to the other members of the nF-16H family of acids, a sample of the
identical acid was also studied with results recorded in Figs. 3, 5, and 7. The results
follow logically those obtained with the other members of this homologous series. Sev-
eral possible causes are suggested why Fox's results are not consistent with the present
ones. Fox used a wax-coated brass film trough which, despite the coating of wax, could
readily have caused contamination of the aqueous substrate by polyvalent metal ions,

especially at higher pH values. Film pressures were measured by the Wilhelmy plate method, in which it is essential that the contact angle on the dipping platinum plate always remain zero; these fluorinated acids adsorb very readily on clean platinum and thus may have affected the contact angle. The solvent used by Fox to spread the monolayers was benzene. Benzene has since been shown by LaMer and coworkers (7,8) to be able to cause a large expansion in the low pressure region of the F-vs-A curve. Because 1F-16H acid monolayers can be compressed only through the expanded portion of the isotherm and collapse shortly after becoming condensed, the nature of the spreading solvent used plays an important role. Hence, the use of benzene by Fox may be responsible for his more highly expanded films than the present ones.

Jarvis, Timmons, and Zisman (13) employing the same equipment and methods as used in the present study have observed monolayers of ω-bromostearic acid spread from solutions in n-hexane on an aqueous substrate of pH 2.2. Their F-vs-A curve is similar to that of 1F-16H acid in the present investigation with respect to the limiting area (A_o), the compressibility, and the pressure at the collapse point; however, their area per molecule at the collapse pressure is $23A^2$ which is smaller than the value of $28A^2$ obtained for the 1F-16H acid. This difference in area is reasonable since the radius of the terminal bromine atom is slightly smaller than that of the $-CF_3$ group.

ELECTRICAL PROPERTIES

In the Helmholtz equation $\Delta V = 4\pi\nu\mu_p$, ΔV is the difference in the electrostatic surface potential between the clean water surface and the surface covered by the monolayer of adsorbed organic molecules, μ_p is the component perpendicular to the water surface of the electrostatic dipole moment per adsorbed molecule, and ν is the number of polar organic molecules adsorbed per unit area. When adsorbed in close packing on the surface of water, the fatty acid dipole has its positive end farthest away from the surface. The progressively fluorinated acids discussed here are adsorbed in close packing with the large dipole arising from the fluorinated group pointed in the opposite direction. If ΔV and μ_p for the fatty acids are given positive values, then for the fluorinated acids discussed here ΔV and μ_p will be shown to be strongly negative.

Quite like the F-vs-A curves, the ΔV-vs-A and μ_p-vs-A curves for each series of fluorinated acids at any one substrate pH fall within a narrow band (Figs. 2-7). The curves also show that the number of carbon atoms in the perfluorocarbon portion of the molecule has only a minor influence on the values of ΔV and μ_p when A at the collapse pressure reaches $30A^2$. As usual ΔV varies nearly linearly with A once the film has become condensed, and it approaches a minimum value as the film approaches the solid state. Table 2 compares these values of ΔV of the various films close to the collapse pressure.

As usual in experiments with ionizable hydrophilic groups, varying the pH of the aqueous substrate caused a variation in ΔV for each polar compound. Many years ago Schulman and Hughes (14) reported that the ionization of the carboxylic group at alkaline pH caused a double layer to form with its moment oppositely directed to that of the undissociated COOH group. More recently Sanders and Spink (15) have studied ionization in fatty acid monolayers on very pure water and have found that in the absence of multivalent ions ΔV decreases linearly with increasing pH. They demonstrated that by itself ionization in the monolayer has a much smaller effect on the surface potential than previously supposed. The graph in Fig. 9 of ΔV vs pH for our stearic acid, observed at the state of packing when A is $21A^2$, is in close agreement with these results of Sanders and Spink. Figure 9 also shows the variation of ΔV with pH for the 7F-16H and 10F-10H acids as representatives for the fluorinated acids. Because of the ionization effect, there is a change in ΔV with pH (as seen in Table 2) and accompanying it there must be a change in the dipole contribution by the COOH group as a function of pH.

Table 2
Limiting Properties of Monolayers Spread on Water

Compound	Lim. Area (A^2/Molecule) A_o	Area at Collapse (A^2/Molecule) A	Pressure at Collapse F (dynes/cm)	Surface Potential Difference at Collapse Pressure ΔV(mv)	Vertical Component of Dipole Moment at Collapse Pressure μ_p (D)
			pH = 2.2		
10F-10H acid	37.5	27.5	55	-815	-0.615
8F-10H acid	37.0	29.9	43	-755	-0.580
7F-10H acid	—	34.5	9 (unstable)	-575	-0.535
7F-16H acid	37.8	30.7	37	-720	-0.580
5F-16H acid	36.7	32.5	23	-680	-0.580
3F-16H acid	32.2	29.3	18 (unstable)	-715	-0.590
1F-16H acid	34.0	28.0	8 (unstable)	-710	-0.530
17H acid	23.8	19.0	25	+375	+0.185
			pH = 5.8		
10F-10H acid	37.5	28.0	53	-930	-0.715
8F-10H acid	36.8	29.0	35	-820	-0.650
7F-10H acid	37.2	33.0	12 (unstable)	-760	-0.665
7F-16H acid	36.0	28.4	41	-850	-0.650
5F-16H acid	36.1	31.7	19	-850	-0.675
3F-16H acid	32.1	28.6	14 (unstable)	-875	-0.665
1F-16H acid	34.0	28.0	6 (unstable)	-830	-0.665
17H acid	23.5	18.5	25	+270	+0.135
			pH = 8.6		
10F-10H acid	37.2	28.0	53	-970	-0.740
8F-10H acid	37.5	30.0	46	-905	-0.740
7F-10H acid	37.0	31.0	35	-895	-0.740
7F-16H acid	37.4	30.8	38	-895	-0.730
5F-16H acid	36.9	33.1	17	-825	-0.710
3F-16H acid	34.0	31.5	7	-880	-0.740
1F-16H acid	36.0	30.5	6	-830	-0.670
17H acid	20.4	19.7	23	+220	+0.123

The value of ΔV obtained here involves the resultant of the moment contributed by the carboxylic acid group and those contributed by the carbon-fluorine bonds. The latter must have a resultant located in or adjacent to the fluorocarbon group and so must be well removed from the aqueous substrate. Since the contribution due to the COOH group diminishes as the pH rises, the net value of ΔV becomes more dominated at higher pH values by the resultant of the dipole contribution due to the C-F bonds. Since the latter is a large negative quantity, it is obvious why ΔV ranges from -700 to -970 mv for the fluorinated acids. Of course, ΔV for films collapsing at low pressures cannot reach such very negative values, as is evident in Figs. 2-7. The behavior of graphs of ΔV vs A and μ_p vs A at the several values of the pH, as shown in Fig. 8 for the 10F-10H acid, is representative of the results obtained with all of the more stable monolayers of these fluorinated acids.

In the last column of Table 2 are the values of μ_p in debyes computed from the Helmholtz equation at values of A close to the collapse pressure. Some differences

Fig. 9 – Dependence of surface potentials on pH for compressed monolayers of fatty acids and partially fluorinated acids

in μ_p are evident among the seven fluorinated acids on any one substrate. However, if one ignores the 1F-16H and 7F-10H acids (because the collapse pressure is too low for these compounds to have fully erected the dipoles) it will be found that μ_p is then independent of the number of carbon atoms in the fluorocarbon chain.

It is now possible to compute the contribution of μ_p arising solely from dipoles in the fluorinated carbon chain. The values of μ_p deduced from the observed values of ΔV for a condensed stearic acid monolayer on water is the vectorial sum of the contribution of vertical components from the COOH group and the hydrogen bonded water molecules attached to it, $\mu_{(COOH)_{aq}}$, and the contribution from the aliphatic chain, $\mu_{C_m H_{2m+1}}$, i.e.,

$$\mu_p = \mu_{(COOH)_{aq}} + \mu_{C_m H_{2m+1}}.$$

Assuming, as is usual, that only the terminal -CH$_3$ group determines the value of μ_p in a paraffin chain (16), $\mu_{C_m H_{2m+1}}$ becomes equal to μ_{CH_3}. Hence

$$\mu_p = \mu_{(COOH)_{aq}} + \mu_{CH_3}.$$

Although uncertainties remain in the literature about the correct value of the vertical component μ_{CH_3}, a value of 0.3 debye (17,18), where the positive direction is pointed from the hydrogen to the carbon atom, has been chosen by many investigators and will be used here. If this vertical moment contribution is subtracted from μ_p, the resulting vertical component of the moment $\mu_{(COOH)_{aq}}$, directed with negative end to water, is
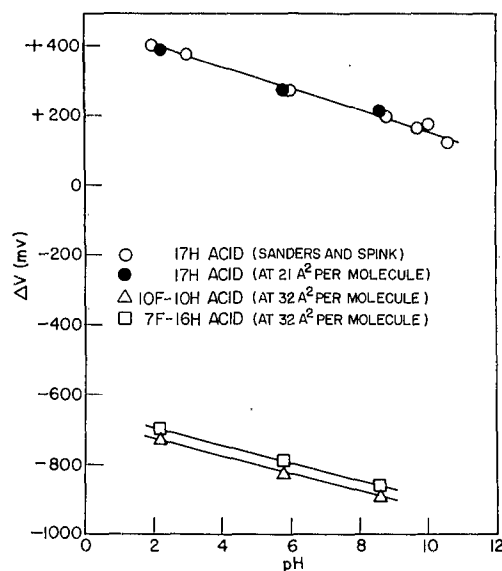
0.090 debyes at a pH of 2.2, 0.160 debyes at a pH of 5.8, and 0.180 debyes at a pH of 8.6. The μ_p of the stearic acid was computed by use of the Helmholtz equation when the molecule is vertically oriented on water (i.e., at an area per molecule of $21A^2$) at the respective pH. Subtracting this value of μ_{COOH} of the carboxylic acid group from the μ_p for each of the fluorinated acids as obtained at a packing of $32A^2$ per molecule for each pH (Figs. 2-7), the resulting vertical component of the moment is that contributed solely by the segmented chain $F(CF_2)_n(CH_2)_m$ and will be denoted as μ_Φ. Hence

$$\mu_p - \mu_{(COOH)_{aq}} = \mu_\Phi .$$

Table 3 gives the values of μ_p and μ_Φ thus obtained for each substrate pH. The resulting μ_Φ is directed with the negative pole up and away from the water.

It can be seen that all values of μ_Φ are nearly constant at each pH regardless of length of fluorocarbon chain segment or hydrocarbon segment. Hence, any contributions to μ_Φ arising from any effect due to the polarization of the water dipoles must be minor; and this would be expected because the fluorocarbon chain segment is about 10A to 20A from the water surface. The maximum 10% variation in μ_Φ with pH, as shown in Table 3, may be a result of a slight change with pH of the orientation of the molecular axis at maximum compression. For vertically oriented molecules in the solid-condensed state, such as stearic acid, ΔV is independent of compression, whereas the fluorine-substituted acids manifest an increase in ΔV with increasing compression.

The value of μ_{CF_3} most accepted in the literature for the vertical component of the -CF_3 dipole moment, based on dielectric constant studies of appropriate compounds in the gaseous state, is 1.9 debyes (19). The values computed here from the properties of the various condensed monolayers on water are all approximately 0.5 debye, or only 1/4 as great. These smaller values of the -CF_3 group moment may be the result of several effects. There may be induced polarization between adjacent fluorocarbon dipoles at the close packing prevalent in a liquid condensed monolayer. There may also be dipole contributions from water molecules which have penetrated between the aliphatic chains in the monolayer. It had been shown repeatedly by many investigators that only highly condensed or solid monolayers can appreciably retard evaporation from the surface of the aqueous substrate. Since a single bromine atom substitution on the ω-carbon atom of stearic acid makes it unable to retard water evaporation (13) whatever the film pressure, the liquid-condensed films of these progressively fluorinated acids will also be unable to prevent evaporation and thus molecularly dispersed water will be present throughout the monolayer. The polarization of such water molecules, especially those nearest the C-F bonds of the fluorinated chain segment, would be expected to decrease μ_Φ.

Only recently Bewig and Zisman (20) have reported values for μ_p of long-chain amines adsorbed on metals which were about half of the reported values obtained from the same compounds in the gaseous state. They explained the smaller values as resulting from the proximity of the polar end groups to the metal surface and the resulting possibility of induced polarization, as well as from another contribution arising from any oriented water dipoles present on the surface of the metal as one or more adsorbed monolayers. The even smaller values obtained in the present investigation are believed to arise in major part from the dipole contribution from water molecules present in the spaces between the oriented aliphatic chains. From the results of the film balance experiments reported here, such water contributions cannot be eliminated even at the collapse pressures of those monolayers because of steric hindrances to molecular adlineation which prevent formation of a solid film.

Table 3

μ_p and μ_Φ of Partially Fluorinated Chains at Area per Molecule of 32A²

$$\mu_p - \mu_{(COOH)_{aq}} \overset{*}{=} \mu_\Phi$$

Fluorinated Compound	pH = 2.2 $\left(\mu_{(COOH)_{aq}} = 0.090D\right)$		pH = 5.8 $\left(\mu_{(COOH)_{aq}} = 0.160D\right)$		pH = 8.6 $\left(\mu_{(COOH)_{aq}} = 0.180D\right)$	
	μ_p (D)	μ_Φ (D)	μ_p (D)	μ_Φ (D)	μ_p (D)	μ_Φ (D)
10F-10H acid	0.610	0.520	0.700	0.540	0.730	0.550
8F-10H acid	0.580	0.490	0.650	0.490	0.730	0.550
7F-10H acid	—	—	—	—	0.730	0.550
7F-16H acid	0.570	0.480	0.650	0.490	0.730	0.550
5F-16H acid	0.570	0.480	0.690	0.530	—	—
3F-16H acid	0.590	0.500	0.680	0.520	0.740	0.560
1F-16H acid	0.540	0.450	0.660	0.500	0.680	0.500

*Area per molecule of 21A² for stearic acid.

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2. Fatty acids –
   Elec. prop.
3. Fatty acids –
   Wettability
I. Bernett, M.K.
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Naval Research Laboratory. Report 5932.
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figs. May 21, 1963.

A study has been made on the force-area, surface
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monolayers of two series of progressively fluorinated
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series were n-heptadecanoic acids with substitutions
in the 17-position of perfluoromethyl, perfluoropropyl,
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at all pH values falls off rapidly with progressively shorter perfluoro segments. The compressed films of all stable acids are in the liquid-condensed state, indicating limiting areas per molecule of $36A^2$ to $38A^2$. The change in surface potentials of all films is larger than those of any aliphatic acid and shows that the dipole is oriented in the opposite direction. By use of the Helmholtz equation the vertical components of the apparent dipole moment were ascertained from the potentials and it was possible to compute, under a given set of conditions, the values of the vertical component of the partially fluorinated chain only. The results were interpreted in terms of orientation and packing of the adsorbed molecules, steric hindrance due to the bulky perfluoro segments, and electrostatic repulsion.